ELECTRICAL SWING REGENERABLE FILTRATION USING CARBON FIBRE COMPOSITES AND CARBON MONOLITHS[1]

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ABSTRACT

The potential of both carbon-bonded carbon fibre composites and phenolic resin based carbon monoliths for regenerable filtration applications in Collective Protection (COLPRO) has been investigated. Both are highly microporous materials and therefore have excellent adsorption properties, in addition, both materials conduct electricity due to their continuous carbon skeletons and therefore can be heated by applying a potential difference across them. Research into identifying the optimum properties required for use of these materials as regenerable adsorbents has been carried out. The results show that for the composites, the adsorption properties are influenced by both the binder content and level of activation. The composite density determines the electrical resistance, and hence the efficiency with which they can be heated for regeneration. The effect of varying the current and time period used for regeneration suggests that a short pulse at higher current regenerates the composite more efficiently than a longer pulse at lower current. The carbon monoliths have excellent adsorption properties with a very low associated pressure drop. Initial studies suggest that they are highly conducting materials with excellent adsorption properties.

1.0 INTRODUCTION

The adsorption properties of a range of carbon-bonded carbon fibre composites and carbon monoliths are currently being investigated for potential use in military filtration applications, particularly regenerable vapour filtration. These materials offer several potential advantages over the granular activated carbons currently employed. For example, they offer improved long-term stability due to reduced attrition, which in turn permits greater versatility in future equipment design. Furthermore, the composites have a continuous carbon skeleton and therefore have high thermal conductivity, as well as being electrically conductive and therefore these materials offer greater potential for regeneration at much lower power.

Regenerable filtration systems currently being tested use pressure and / or temperature swing adsorption, based on the use of granular adsorbent media. The energy requirements of these systems results in a significant burden, particularly for use on armoured fighting vehicles (AFVs). The potential use of carbon composites for regenerable filtration offers scope for reducing this power requirement. They can be directly heated through resistive heating, and the present research is focusing on a purely electrical swing process, without the need for a pressure swing cycle.

The carbon-bonded carbon fibre composites described in this paper were prepared at LexCarb (formerly Advanced Separation and Adsorption Products), 3130 Lamar Drive, Lexington, Kentucky, USA. The phenolic resin-based carbon monoliths described in this paper were prepared by MAST Carbon Ltd, Guildford, UK.

This paper describes initial studies into the applicability of carbon-bonded carbon fibre composites and phenolic resin-based carbon monoliths for regenerable filtration applications. The initial characterisation of these materials will be described, as will the adsorption properties. For the carbon composites initial studies into their ability to undergo regeneration have been carried. For the carbon monoliths only the dynamic adsorption properties have been assessed at the present time.

2.0 EXPERIMENTAL

2.1 Samples

2.1.1 Carbon-bonded carbon fibre composites

The carbon composites were prepared from an aqueous slurry of chopped carbon fibres with a phenolic resin as a binder. The binder content of the samples varied from 10 to 33 % w/w. The mixture was formed into cylinders and then dried and cured in an oven at temperatures up to 200^{o}C. The composites were then carbonised and finally activated to varying extents in a 50:50 nitrogen:steam atmosphere at 870^{o}C. The activation process was carried out in order to introduce porosity into the composite. The diameters of the composites described were *ca.* 2.5 cm; the composites were cut to the length required for each experiment. A typical section of composite is shown in Figure 1.

Figure 1. Carbon-bonded carbon fibre composite.

2.1.2 Carbon monoliths

The monoliths were prepared from a phenolic resin precursor[1] and following carbonisation possess a nitrogen BET surface area of approximately 600 $m^2 g^{-1}$. Selected monolith samples have been further activated, increasing the surface area to *ca*. 1000 $m^2 g^{-1}$. The two types of sample are referred to in the text as "carbonised" or "activated" respectively to distinguish their use in this study.

Each monolith sample is comprised of a 3 cm diameter cylinder containing continual longitudinal square channels approximately 1 mm across, separated by carbon walls of approximately 0.8 mm thickness. The monoliths introduce only a minimal resistance into the air flow, offering the potential to provide significant levels of protection with a very low associated pressure drop. Examples of monolith sections are illustrated in Figure 2.

Figure 2. Carbon monolith.

2.2 Characterisation techniques

2.2.1 Burn-off

During the activation process, the materials decrease in mass. This decrease, as a percentage, gives an indication of the level of activation. For the carbon composites the burn-off values were calculated by LexCarb.

2.2.2 Pressure drop

The pressure drop across the materials was measured whilst the samples were in the filter line prior to testing. The pressure drop was measured at a variety of different flow rates. Measurements were made using a digital manometer (Digitron P200UL).

2.2.3 Static adsorption studies

Nitrogen isotherms - nitrogen adsorption isotherms were measured at -196°C, using an automated instrument (Omnisorp 360, Coulter Electronics Ltd.). Specific surface areas were derived from the isotherms using the BET equation[2].

Water isotherms - the hydrophilicity of the materials was determined by water adsorption using an automated instrument (CISORP95, C I Electronics Ltd.). Approximately 75 mg of material was placed in a mesh container that was suspended from a microbalance. The sample was then equilibrated at various relative humidities ranging between 10 and 90% at 22°C. The water adsorption, as a percentage of the dry adsorbent weight, was calculated for each step of the isotherm from the recorded weight data.

Hexane isotherms - hexane adsorption isotherms were determined using a Hiden Analytical Intelligent Gravimetric Analyser (IGA-1). The sample size was 70-100 mg, and the isotherms were measured at 22 ºC.

2.3. Dynamic adsorption testing

Dynamic filter testing was carried out in order to ascertain the ability of either the composite or the monolith to remove a physisorbed challenge from flowing air. Short sections of material were mounted in "heat-shrink tubing" and mounted into a small-scale filter test apparatus, illustrated in Figure 3. This assembly enabled both the composite and monolith samples to be "challenged" with test vapours under carefully controlled conditions of temperature, humidity, concentration and flow rate.

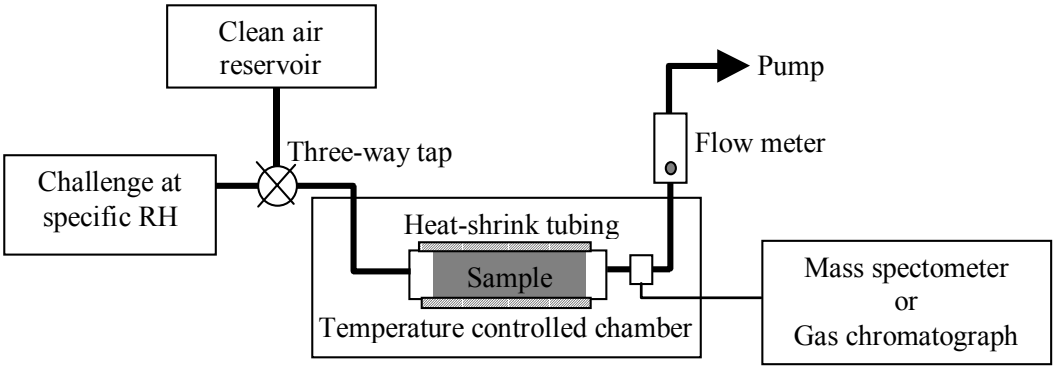

Figure 3. Small scale filter test apparatus.

For each of the tests, the challenge was passed through the material at 1 l min^{-1}. The efficiency of each material to remove the challenge was determined by the time taken for the challenge gas to be detected in the effluent (*ca.* 1% of the influent concentration). The effluent was monitored using a gas chromatograph (Chrompack CP9001) fitted with a flame ionisation detector, or mass spectrometer, calibrated before each test using the challenge mixture.

The materials were assessed for their ability to remove a variety of physisorbed challenges including butane, hexane and octane. These were of varying concentration and were prepared by passing either humid (80% RH), or dry (<5% RH), air over the corresponding weight of the specified challenge for a specific duration at a flow rate of 5 l min^{-1}. The mixture was then blended thoroughly.

2.4 Regenerable filter testing

Samples were mounted in heat shrink tubing and placed in the small-scale test apparatus described above. The samples were then exposed to octane vapour (8000 mg m^{-3}) for varying times at a flow rate of 1 l min^{-1} in RH 80% air at 22 °C. The effluent airstream was monitored using a quadrupole mass spectrometer (tuned to m/z = 57; $CH_3(CH_2)_3^+$). The composites were regenerated by reversing the flow (1 l min^{-1}) and passing a current through each. At the start of the regeneration, the potential difference required to achieve this current was noted, and the resistance calculated according to Ohm's law. A thermocouple was mounted in the effluent end of the composite to monitor the temperature. The direction of the air flow dictates that this is the region of highest temperature.

A 6 cm length section of carbon composite was mounted in the small-scale filter test apparatus and repeated adsorption / desorption cycles were carried out. The challenge was stopped as soon as octane was detected in the effluent (detection limit < 1 % of the influent level). The flow direction was reversed and the composite was regenerated in a flow of 1 l min^{-1} dry (RH<5%) air using carefully selected conditions of electrical current and time duration. Thermocouples located in each end of the composite were monitored during regeneration. At higher currents, the duration of the pulse was limited by the necessity to avoid heating the composite assembly to above 150ºC, a restriction imposed by the heat-shrink tubing in which the composite was mounted. The breakthrough time on the following adsorption test was used to assess the extent to which the carbon had been regenerated.

3.0 RESULTS AND DISCUSSION

3.1 Carbon-bonded carbon fibre composites

3.1.1 Samples

The bulk densities of the carbon-bonded carbon fibre composites are summarised in Table 1. Italicised symbols in brackets are used later in this report to refer to specific samples (*e.g. 2B* represents a composite with 20% binder, 20% burn off, comprised of 67% P400:33% P200T carbon fibres). The P400 fibres were shorter than the P200T fibres.

TABLE 1. Bulk densities of carbon composite samples / g cm^{-3}

Binder content (%) / Burn off (%)	Fibre ratio P400:P200T			
	100:0 *(1)*	67:33 *(2)*	33:67 *(3)*	0:100 *(4)*
33 / 10 *(A)*	0.23	0.28	0.36	0.44
20 / 20 *(B)*	0.18	0.23	0.29	0.37
10 / 30 *(C)*	0.15	0.20	0.25	0.31

The data in Table 1 illustrates that as the proportion of shorter fibres increases, then the density of the resulting composite is higher. This is consistent with the fibres packing more closely. It can also be seen that reducing the binder content and increasing the burn-off causes the density to be reduced, as expected.

3.1.2 Static adsorption studies

3.1.2.1 Nitrogen adsorption isotherms

Data derived from the nitrogen adsorption isotherms is summarised in Table 2.

TABLE 2. Data derived from nitrogen adsorption isotherms

Sample reference	Specific surface area ($m^2 g^{-1}$)	External surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Mesopore volume ($cm^3 g^{-1}$)	Micropore volume ($cm^3 g^{-1}$)
1A	700	46	0.295	0.066	0.229
1B	973	37	0.378	0.051	0.327
1C	1151	66	0.516	0.085	0.431
2A	787	17	0.300	0.029	0.271
3A	817	21	0.313	0.033	0.280
4A	899	35	0.352	0.051	0.301
4C	1109	31	0.472	0.041	0.431

Nitrogen adsorption data (Table 2) shows that as the binder content is reduced and burn off increased, the surface area increases (see for example series *1A – 1C*). Comparison of sample series *1A – 4A* suggests an increase in surface area as the fibre length is reduced; this is not expected and it should be noted that samples *1C* and *4C* do not confirm the trend. The samples are all predominantly microporous, although some of them do also possess significant mesoporosity.

3.1.2.2 Water and octane adsorption isotherms

No significant differences between samples prepared using different fibre lengths were noted. The effect of varying binder content and burn off on water adsorption capacity is summarised in Table 3 in terms of their uptakes at RH 95%. Mean values of each series are listed with standard deviations.

TABLE 3. Water adsorption capacities of carbon composite samples

Composite series	Water uptake at RH 95% (w/w% ± sd)
A	18.0 ± 0.7
B	23.6 ± 2.1
C	31.6 ± 2.6

All isotherms were Type V according to the IUPAC classification[2], as expected from predominantly microporous adsorbents. The adsorption uptakes of octane after 24 hours exposure are listed in Table 4. As with the water adsorption, no significant trends were noted as the fibre length varied, and thus the data are presented in an analogous format to that in Table 3.

TABLE 4. Octane adsorption capacities of carbon composite samples

Composite series	Octane adsorption capacity (w/w% ± sd)
A	15.5 ± 0.3
B	19.3 ± 1.1
C	26.5 ± 1.4

The samples were replaced in the desiccator after weighing, but showed no significant increase in uptake after further exposure.

3.1.3 Dynamic adsorption performance

3.1.3.1 Pressure drop

The variation in pressure drop with burn-off for carbon composites with 20 % w/w binder are shown in Table 5.

TABLE 5. Variation in pressure drop with burn-off for composites with 20 % w/w binder

Burn off (%)	Maximum water uptake at 90% RH (w/w %)	Pressure drop (inches water at 1.4 l min^{-1})
10	15.8	2.85
20	21.1	2.84
30	36.0	2.67
40	36.0	2.74

The pressure drop of the samples does not vary significantly, although the higher burn off samples tend to show the lowest values. This is probably due to the higher voidage caused by the reduced amount of carbon in these samples.

3.1.3.2 Dynamic removal of physisorbed challenges

The performance of the carbon composites with 20 % w/w binder is shown in Table 6. The results show that removal of hexane (4000 mg m^{-3}) is good. Hexane is a physically adsorbed vapour with a boiling point of 69ºC. The results show that, as expected, the performance of the carbon composite for removing hexane is better in dry conditions compared to humid. This is because under humid conditions, the hexane must first displace the pre-adsorbed water from the surface of the carbon before it can be adsorbed.

TABLE 6. Variation in time to 1 % breakthrough of hexane with burn-off for carbon composites with 20 % w/w binder under dry (RH<5%) and humid (RH80%) conditions

Burn-off (%)	Time to 1 % breakthrough of hexane (mins)	
	Dry (RH < 5%)	Humid (RH80%)
10	37	10
20	39	33
30	16	34
40	39	31

3.1.4. Regenerable filter testing

3.1.4.1 Initial studies

Table 7 lists the initial resistances of the composite samples and the temperature recorded after passing a current of 3A for one minute at 1 l min^{-1} (samples referenced as described earlier).

TABLE 7. Electrical resistance (Ω) / temperature after one minute (°C) for carbon composites during regeneration

Sample references	*1*	*2*	*3*	*4*
A	0.74 / 32.2	0.90 / 35.8	0.74 / 35.2	0.58 / 27.7
B	1.77 / 58.8	1.18 / 40.0	1.22 / 48.9	0.85 / 46.8
C	3.25 / 71.1	1.99 / 59.8	1.83 / 62.9	1.45 / 68.2

Table 7 illustrates that the resistance of the composites is related to their density. The overall trend is that the higher the composite density, the lower the resistance. This is consistent with a greater number of inter-fibre contacts in the more dense composites. According to the Joule effect, this resistance impacts on the temperature achieved when a potential difference is applied, as reflected in the data.

Table 8 summarises the efficiency with which octane can be desorbed from the composite samples. Each composite was challenged and then regenerated as described in section 2.4. The values in the table compare the amount desorbed to the amount adsorbed, expressed as a percentage. Therefore, the higher values represent the composites that are easiest to regenerate.

TABLE 8. Octane "desorption efficiency" during regeneration / %

Sample references	*1*	*2*	*3*	*4*
A	32.2	35.8	35.2	27.7
B	58.8	40.0	48.9	46.8
C	71.1	59.8	62.9	68.2

The octane desorption efficiencies in Table 8 show, as expected, that those composites which achieve higher temperatures desorb the most octane.

Overall, careful study of the data reveals the extent to which the properties of these composites can be tuned to meet the user's requirements. Inspection of the sample densities contained in Table 1 reveals several series of samples which have similar densities (*e.g. 1A*, *2B*, *3C*, or *2A*, *3B*, *4C etc*.), but are prepared via different methods. This impacts on their adsorption and electrical properties, as cross-reference to later data confirms. The adsorption properties are predominantly influenced by the binder content and level of activation, but not by the fibre length. This offers two methods of varying composite density, only one of which affects the adsorption properties. The materials therefore give scope for selecting not only the adsorption properties, but also the mechanical properties required for each application.

3.1.4.2 Further studies

Table 9 summarises the results from further studies into the regeneration of carbon composites. Regeneration conditions and temperature rises are self-explanatory; the breakthrough time quoted is that for the challenge immediately after regeneration under the specified conditions (and is thus indicative of the extent of regeneration achieved). The composites used in this study were all of the *2A* kind, described previously.

TABLE 9. Temperature rise and breakthrough time achieved for various electrical energy profiles

Current (Amps)	Time/ t (minutes)	Electrical energy (kJ)	Influent temperature rise after (t) minutes (ºC)	Effluent temperature rise after (t) minutes (ºC)	Breakthrough time (minutes)
Time constant for varying currents					
0	n/a	0	n/a	n/a	8.5 ± 0.6
1	15	0.6	-0.1	3.6	6.9
2	15	2.1	1.1	13.9	8.5
3	15	4.8	4.0	32.5	12.5
4	15	8.4	9.4	65.7	17.5
5	15	13.6	19.6	98.2	23.7
6	15	18.4	30.2	125.3	34.0
Current constant for varying times					
6	10	12.6	28.5	128.5	27.0
6	5	6.2	23.2	110.9	23.4
6	2	2.5	11.7	60.2	14.3
Higher currents for shorter times					
7	2	3.5	21.6	93.5	17.5
8	2	4.3	25.8	113.4	21.6
9	1	2.7	11.4	83.9	15.2

Regenerable filtration systems currently being tested use pressure and / or temperature swing adsorption, based on the use of granular adsorbent media. The energy requirements of these systems results in a significant burden, particularly for use on armoured fighting vehicles (AFVs). The potential use of carbon composites for regenerable filtration offers scope for reducing this power requirement. They can be directly heated through resistive heating, and the present research is focusing on a purely electrical swing process, without the need for a pressure swing cycle.

The data in Table 9 illustrates the importance of optimising the electrical parameters in order to achieve the maximum efficiency. The most efficient regeneration is observed from regeneration with relatively high currents for relatively short periods. This can be seen, for example, by comparing the data for 4A / 15 minutes with that for 7A / 2 minutes. The subsequent breakthrough times are identical, but the energy input in the latter case is less than half that in the former. This effect is beneficial in that it enables the time for regeneration to be minimised, therefore reducing limitations on the cycle time which can be used.

Although the data suggests that regeneration for 15 minutes at 1 A makes the breakthrough time shorter, this is probably a reflection of the experimental error associated with these tests. It is assumed that regeneration at 1 A or 2 A is in fact causing no further octane to desorb compared with regeneration at ambient temperature. This is because the temperature rises in the composite are relatively low under these conditions. It should be noted that these test conditions are relatively arbitrary, but they illustrate that careful selection of regeneration parameters will be a significant consideration in determining the overall energy requirement of electrical swing regeneration systems.

3.2 Carbon monoliths

3.2.1 Static adsorption studies

3.2.1.1. Nitrogen adsorption isotherms

Carbonised monoliths were reported by MAST Carbon Ltd to have nitrogen specific surface areas of around 500-600 m^2 g^{-1}. Specific surface areas for activated samples (derived from the isotherms using the BET equation) were typically double those reported for carbonised samples. Analysis using the α_s method showed that the monoliths were predominantly microporous.

3.1.2.2 Water and hexane adsorption isotherms

The water adsorption isotherms at 22 ^oC for both the carbonised and activated carbon monoliths are shown in Figure 4.

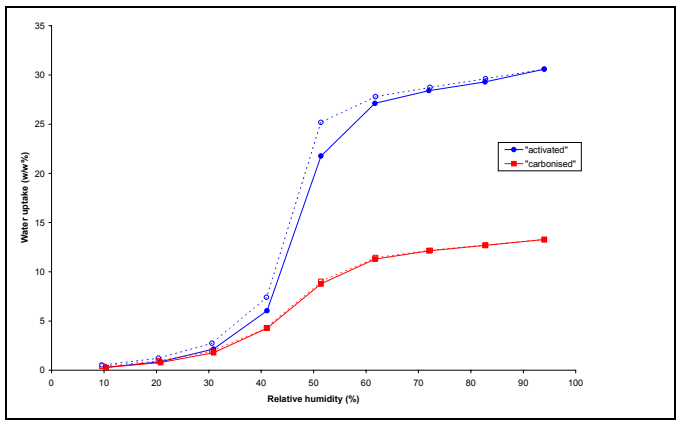

Figure 4. Isotherms for the adsorption of water on both the carbonised and activated carbon monoliths at 22 ^oC. (solid lines – adsorption; dotted lines – desorption)

Both the carbonised and activated monolith water isotherms are Type V according to the IUPAC[2] classification, this being characteristic of microporous adsorbents. Unusually however, they exhibit narrow hysteresis loops, which may be caused by the pore shape in these carbons. The pore shape is believed to comprise of voids between spherical particles[1]. This hysteresis is also indicative of a lack of mesoporosity in these adsorbents.

The hexane adsorption isotherms for both the carbonised and activated monolith samples are illustrated in Figure 5.

The activated monolith sample exhibits a higher adsorption capacity for hexane, which is consistent with the higher surface area and pore volume as determined by nitrogen adsorption. However, close examination of the data revealed that the adsorption kinetics was also substantially improved as a result of activation. Table 10 compares data acquired during the first adsorption stage of the isotherm (P/P_o ~ 0.01).

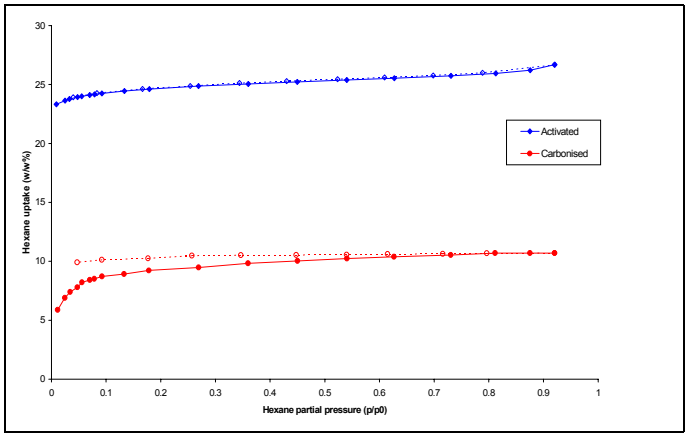

Figure 5. Isotherms for the adsorption of hexane on both the carbonised and activated carbon monoliths at 22 ^oC. (solid lines – adsorption; dotted lines – desorption).

TABLE 10. Adsorption kinetics comparison for carbonised and activated monoliths

Monolith sample	Equilibrium adsorption capacity at $P/P_o \sim 0.01$ (w/w%)	Time taken to achieve equilibrium loading (minutes)
Carbonised	6.4	>600
Activated	23.3	<10

It can be seen that under these conditions, activation not only results in an increased adsorption capacity, but also causes a substantial increase in the rate of adsorption. Compared on a "mass per time" basis, the latter increase is of the order of 200 fold.

3.2.2 Dynamic adsorption performance

3.2.2.1 Pressure drop

For all samples tested (*i.e.* up to 12 cm length), the pressure drop at 2 l min^{-1} flow was below measurable levels using the method described in section 2.2.2.

3.1.4.3 Dynamic removal of physisorbed challenges

The ability of a 2 cm carbonised carbon monolith to remove hexane (2 l min^{-1}, 22 ºC, 8000 mg m^{-3} influent concentration) under both dry (RH<5%) and humid (RH80%) conditions was studied. The breakthrough times (time taken for the effluent concentration to reach 1% of the influent) were 100 minutes and 40 minutes respectively. This represents remarkable adsorption performance from this length of monolith especially taking into account that the adsorbent has essentially no pressure drop at these flow rates.

Following the successful removal of hexane the lower boiling butane was investigated. Figure 5 compares the butane breakthrough curves for both carbonised and activated sections of monolith challenged with 8000 mg m^{-3} butane (7 cm length, 3 cm diameter, 2 l min^{-1} flow, 22 ºC, RH<5%)

The discontinuities in the carbonised breakthrough profile of Figure 6 are caused by brief interruptions to the influent vapour stream to replenish the challenge source. It can be seen that a small, relatively constant concentration of butane (*ca*. 5% of the influent level) is present in the effluent almost from the start of the test. This shows that a small proportion of the molecules travel through the monolith channels without being adsorbed. The effluent concentration does not rise significantly above this level until around 100 minutes after the start of the test, showing that the monolith does possess a significant adsorption capacity for butane. However, the "leak effect" clearly has important implications for use of these materials in NBC applications. However, looking at the breakthrough profile for the activated monolith shows no

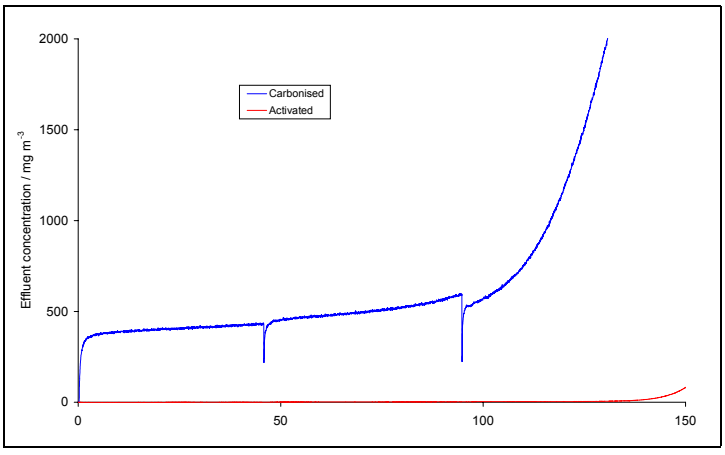

Figure 6. Breakthrough curve for butane through 7 cm length of carbonised and activated, monolith at 22 ºC.

significant leakage of butane during the test, as well as demonstrating a higher overall adsorption capacity. This suggests that the collisions between the adsorptive molecules and the carbon are more likely to result in adsorption in the activated section compared to the carbonised monolith.

The data clearly show that activation of the monolith removes the leak concentration, leaving a breakthrough time in excess of 140 minutes, which again represents significant adsorption of this relatively volatile adsorptive.

Having demonstrated that carbon monoliths can be prepared which adsorb without leakage further work is currently being carried out to investigate their use in regenerable filtration applications. This will focus on the use of direct electrical heating to regenerate the adsorbents, capitalising on the fact that the monoliths are excellent electrical conductors.

CONCLUSIONS

A series of carbon bonded carbon fibre composites with varying densities has been studied. It is apparent that the preparation conditions influence both the adsorption and electrical properties. The adsorption properties are significantly affected by the binder content and level of activation. In terms of electrical properties, samples of higher density offer lower electrical resistance and therefore are more difficult to heat than samples of lower density. High current, short duration, pulses of electrical power result in more efficient regeneration of the composite than do low current, longer duration pulses. Overall, the results show that carbon composites offer excellent potential as adsorbents for regenerable filtration applications and their properties can be tuned according to the user's requirements.

Phenolic resin-based carbon monoliths have been shown to possess remarkable adsorption properties, even when tested at very short lengths. This coupled with the very low associated pressure drop clearly demonstrates their potential for use in a range of adsorption applications. Small leaks have been observed in carbonised monoliths for certain highly volatile species, *i.e.* butane. Monolith activation, however, enhances adsorption capacity and kinetics leading to a significant reduction in monolith leak effects, thus increasing their filtration performance. Studies are currently underway to assess the ability of these materials to undergo regeneration.

REFERENCES

1. Tennison S.R. Applied Catalysis A:General 1998:173;289-311

2. Gregg S.J. & Sing K.S.W., Adsorption Surface Area and Porosity; Academic Press 1982

ACKNOWLEDGEMENTS

The authors would like to thank the UK MOD for funding this research